gioselectivity with the electron population obtained by natural orbital analysis may be of some use in predicting the regioselectivity of carbometalation reactions. In the light of the data presented above, the carbometalation reaction may be viewed to involve both an electrophilic attack of the metal and a nucleophilic attack of the alkyl group taking place simultaneously. It may thus be qualitatively stated that polarization of the acetylene group directed by mesomeric electron donation from oxygen or nitrogen group and inductive influence of the sulfur or silicon group determines the regiochemistry of the carbometalation reaction. In addition, it is very likely that the same principle operates for the heteroatom-substituted olefin.[12-14] (4) Success of the present theoretical analysis suggests that simple monomeric metal models may be useful for the understanding and designing[6b] of carbometalation reactions. The deficiency of the metal environment may be cancelled by judicious setup of reference models for comparative evaluation.

Acknowledgment. We thank Drs. M. Isaka and B. H. Lipshutz for helpful discussions and M. Nakamura for some computational work. Financial support from the Ministry of Education, Science and Culture and the Asahi Glass Foundation is gratefully acknowledged. A generous allotment of computer time from the Institute for Molecular Science is deeply appreciated.

Supplementary Material Available: Listings of optimized geometries (*Z*-matrices) of π-complexes, TSs, and products and the EDA data for MeCu and MeLi additions to CH_3- and SiH_3-substituted acetylenes (34 pages). Ordering information is given on any current masthead page.

On the Mechanism of the Zirconium-Catalyzed Carbomagnesation Reaction. Efficient and Selective Catalytic Carbomagnesation with Higher Alkyls of Magnesium

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Abstract: In zirconium-catalyzed carbomagnesation of alkenes, the dramatic enhancement in reactivity and selectivity induced by an internal Lewis base is such that higher order alkylmagnesium halides, normally significantly less reactive than EtMgCl, may be used efficiently. In reactions with *n*-BuMgCl, two secondary carbon stereogenic centers are formed with excellent levels of stereocontrol (**4**, >95%). Experimental data are presented which demonstrate that the observed levels of selectivity and reactivity are not simply the result of regioselective insertion of the alkene into the zirconacyclopropane. A general mechanism scheme for carbomagnesation of bicyclic substrates **1** is presented. Noteworthy mechanistic issues are the following: (1) Excess alkylmagnesium halide is required for high levels of regioselectivity and substrate reactivity. We suggest that the influence of the Grignard reagent stems from generation of the zirconate complex **12** (R = H, Me, or Et), which may be more susceptible to ligand exchange than its zirconacyclopropane precursor **7**. Subsequent formation of the zirconocene complex of the reacting alkene would then lead to the high levels of reactivity and selectivity observed in reactions where excess alkylmagnesium halide is present. (2) Deuterium labeling experiments demonstrate that the resident Lewis base strictly controls and reverses the mode of metallacyclopentane cleavage. The heteroatom binds and delivers magnesium to initiate a highly regioselective metallacyclopentane cleavage, effecting a Mg–Zr exchange with inversion of configuration.

Recent studies from these laboratories have demonstrated that Cp_2ZrCl_2 effectively catalyzes the addition of EtMgCl to unactivated alkenes with excellent levels of regio- and stereocontrol.[1] Internal Lewis bases were shown to enhance significantly the utility of the catalytic carbon–carbon bond-forming reaction. Herein, we report the results of our studies on the mechanism of the zirconium-catalyzed carbomagnesation of cyclic homoallylic alcohols and ethers. Alkenes **1** were selected as initial mechanistic probes for their rigid structure and olefin substitution pattern (to study regioselectivity; terminal alkenes invariably afford a primary C–Mg bond). Our work employs variations in reaction efficiency and selectivity (both regio and stereo) to shed light on several of the salient features of the reaction pathway. We find that, although metallacyclopentanes are likely intermediates,[2] simple insertion of the reacting alkene into the zirconacyclopropane does not account for the reported levels of selectivity and reactivity.[1]

In connection to our mechanistic studies, we have explored catalytic carbomagnesations with longer chain alkylmagnesium halides. We find that the enhancement in reactivity and selectivity induced by an internal Lewis base is such that these alkylmagnesium halides, normally significantly less reactive than EtMgCl,[3] can also be used in the metal-catalyzed process. Whereas reactions of *exo*-5-norbornen-2-ol with *n*-PrMgCl and *n*-BuMgCl yield ≤15% of the two exo alkyl isomers nonselectively, *endo*-5-norbornen-2-ol (5 equiv of *n*-alkylMgCl, 10 mol % Cp_2ZrCl_2, 25 °C) affords **2** or **4** in >99% regioselectivity and >85% yield (Tables I and II).[4] Noteworthy is the fact that with *n*-BuMgCl, as is shown in Table II, two secondary carbon stereogenic centers are formed with excellent stereocontrol (**4**, >95%).[5] When the hydroxyl group is protected as its MEM ether,[6] or with

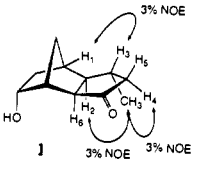
(1) (a) Hoveyda, A. H.; Xu, Z. *J. Am. Chem. Soc.* **1991**, *113*, 5079–5080. (b) Hoveyda, A. H.; Xu, Z.; Morken, J. P.; Houri, A. F. *J. Am. Chem. Soc.* **1991**, *113*, 8950–8952.

(2) Zirconacycles have been suggested as intermediates in carbomagnesation. See: (a) Reference 1. (b) Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 6266–6268. (c) Knight, K. S.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6268–6270. (d) Lewis, D. P.; Muller, P. M.; Whitby, R. J.; Jones, R. V. H. *Tetrahedron Lett.* **1991**, *32*, 6797–6800.

(3) Dzhemilev, U. M.; Vostrikova, O. S. *J. Organomet. Chem.* **1985**, *285* 43–51.

(4) All compounds reported herein gave ^1H NMR, ^{13}C NMR, IR and combustion analysis data/high-resolution mass spectra consistent with the structures given.

(5) The stereochemical outcome of the carbomagnesation with higher alkyls of magnesium was determined through NOE difference experiments on the tricyclic ketone **I**, derived from reaction of **1a** with $Cp_2Zr(n\text{-}Pr)_2$ and 200 mol % *n*-PrMgCl, followed by CO quench (see the Experimental Section for further details). Irradiation of H_1 leads to 3% enhancement of H_3, and H_6 shows a 2.0 Hz *W*-coupling with H_4 (and not H_5); irradiation of CH_3 results in 3% enhancement of H_4 and H_2, but none of H_5.



1

(6) Abbreviation: MEM = $CH_3OCH_2CH_2OCH_2$.

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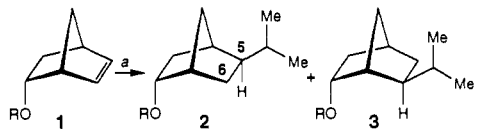
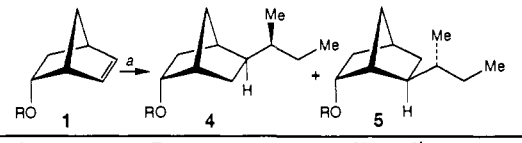
Table I. Regiocontrol in Catalytic Propylmagnesation of **1**



substrate	R	solvent	% yield[b]	2:3[c]
1a	H	Et_2O	88	>99:1
		THF	83	97:3
1b	MEM	Et_2O	40	96:4
		THF	40	75:25

[a] 4 equiv of *n*-PrMgCl, 10 mol % Cp_2ZrCl_2, 40 h; 10% HCl at 0 °C. [b] Isolated yields of purified products. Mass balance >95% in all cases. [c] Ratios determined by GLC analysis (of acetates in case of **1a**).

Table II. Regio- and Diastereocontrol in Catalytic Butylmagnesation of **1**

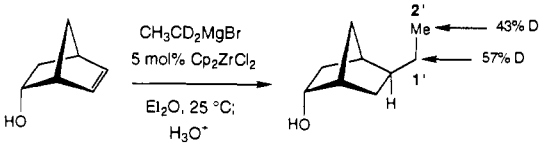


substrate	R	solvent	% yield[b]	4:5[c]
1a	H	Et_2O	86	>99:1
		THF	80	98:2
1b	MEM	Et_2O	30	96:4
		THF	27	67:33

[a] 4 equiv of *n*-BuMgCl, 10 mol % Cp_2ZrCl_2, 40 h; 10% HCl at 0 °C. [b] Isolated yields of purified products. Mass balance >95% in all cases. [c] Ratios determined by GLC analysis (of acetates in case of **1a**).

THF as solvent,[7] chelation is altered and inferior yields and selectivities are obtained. The data in Tables I and II are similar to those recently reported by us for carbomagnesations with EtMgCl;[1b] these findings further support the contention that internal chelation is central to reaction efficiency and selectivity in transition metal-catalyzed carbomagnesation.

Association of zirconocene to the olefin and the heteroatom (**6**, Scheme I) may account for the positive influence of the endo oxygen in carbomagnesations of **1**. One plausible mechanism is that, when the metal shifts to the alkene terminus proximal to the oxygen atom (C6),[8] the slippage leads to distortion of the zirconacyclopropane and activation of the metal–olefin complex, culminating in the formation of the carbon–carbon bond at the distal carbon, C5 (for a more detailed discussion of heteroatom–metal interaction, see below). The alkylating agent may then be introduced as the alkylmagnesium reagent or as an alkylzirconium. As is shown in eq 1, treatment of **1a** with 5 equiv of CH_3CD_2MgBr (5 mol % Cp_2ZrCl_2, Et_2O) results in significant scrambling of deuterium (57:43, *d*-Cl′:*d*-C2′; ^2H and ^{13}C NMR analysis).[9] These data, and the fact that reactions with *n*-PrMgCl and *n*-BuMgCl afford isopropyl and *sec*-butyl adducts, respectively, demonstrate that under *catalytic* conditions, as illustrated in



(1)

Scheme I, the alkyl group is introduced as a zirconacyclopropane (**7**, Scheme I).[2]

The mechanism proposed in Scheme I reserves a critical role for the transition metal: olefin activation and control of selectivity through the zirconocene complex of the reacting alkene (e.g., **6**). Two features of this pathway are notable and merit elaboration.

(1) Origin of Enhanced Reactivity and Selectivity. Reaction of the Mg salt of **1a** with 1 equiv of Cp_2ZrEt_2 or $Cp_2Zr(n\text{-}Pr)_2$ (25 °C, 3 h, THF), precursors to zirconacyclopropanes (**7**, R = H or Me),[10] affords the desired products with only 70:30 selectivity (C5:C6 alkylation) in 35–60% yield.[11] This is in contrast to the 97:3 selectivity and 85% yield that is obtained under the catalytic conditions.[1b] Such striking discrepancy in selectivity and efficiency[12] between the catalytic and stoichiometric conditions is either the result of the variation in the relative amounts of **1**:zirconacyclopropane **7** (1:1 (stoichiometric) versus 10–20:1 (catalytic)) or arises from the presence of excess alkyl Grignard reagent. In connection to the first scenario, carbomagnesation of the Mg salt of **1a** with 25, 50, 100, 200, and 400 mol % Cp_2ZrEt_2 or $Cp_2Zr(n\text{-}Pr)_2$ consistently leads to the formation of a 70:30 ratio of regioisomers. However, as is illustrated in Table III, with 1 equiv of Cp_2ZrEt_2 or $Cp_2Zr(n\text{-}Pr)_2$ and additional alkylmagnesium chloride, selectivity begins to increase steadily: *it is the excess alkylmagnesium halide that is required for high levels of substrate reactivity and that renders the catalytic reactions selective.*

Table III. Influence of Excess Alkylmagnesium Chloride on Regioselectivity in Carbomagnesation of **1a** with Dialkylzirconocenes

% excess RMgCl	alkylation regioselectivity[a] cond A C5:C6	cond B C5:C6	% conversion[b] cond A	cond B
0	70:30	70:30	35	60
50	82:18	85:15	75	83
100	95:5	92:8	95	90
200	97:3	96:4	100	94

[a] Ratios of alkylation at respective carbons, determined by GLC analysis of acetates. Condition A(B): With 1 equiv of Cp_2ZrEt_2 ($Cp_2Zr(n\text{-}Pr)_2$) and the indicated amount of EtMgCl(*n*-PrMgCl) at 25 °C (18 h, THF). [b] Determined by GLC analysis.

It may be argued that formation of the metallacyclopentane under both catalytic and stoichiometric conditions is selective, but that without additional alkylmagnesium halide there is no cleavage of **8** and the metallacyclopentane undergoes equilibration,[13] leading to lower levels of selectivity. Various experimental data show that this is not the case. When **1a** is treated with 1 equiv of $Cp_2Zr(n\text{-}Pr)_2$ and 200 mol % of *n*-PrMgCl (cond B, Table III) and the reaction is quenched with D_2O/D_2SO_4 (18 h), **2a** is formed with 96:4 selectivity; ^{13}C and ^2H NMR spectra indicate >95% deuterium incorporation at C2′ and C6 (exo D). Thus, zircona-

(7) For representative examples where THF alters selectivity, presumably through its deleterious influence on internal chelation, see: (a) (Involving Li) Overman, L. E.; McCready, R. J. *Tetrahedron Lett.* **1982**, *23*, 2355–2358. (b) (Involving Mg) Keck, G. E.; Boden, E. P. *Tetrahedron Lett.* **1984**, *25*, 265–268.

(8) (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308–4320. (b) Fujimoto, H.; Koga, N. *Tetrahedron Lett.* **1982**, *23*, 4357–4360.

(9) The observed secondary isotope effect (relative deuterium enrichment at Cl′, $k_H/k_D \approx 0.86$) indicates preferable alkene insertion into the deuterated carbon–Zr bond. This observation implies that the C–C bond-formation step involves a relatively late transition state (and thus a distorted metal–alkene complex).

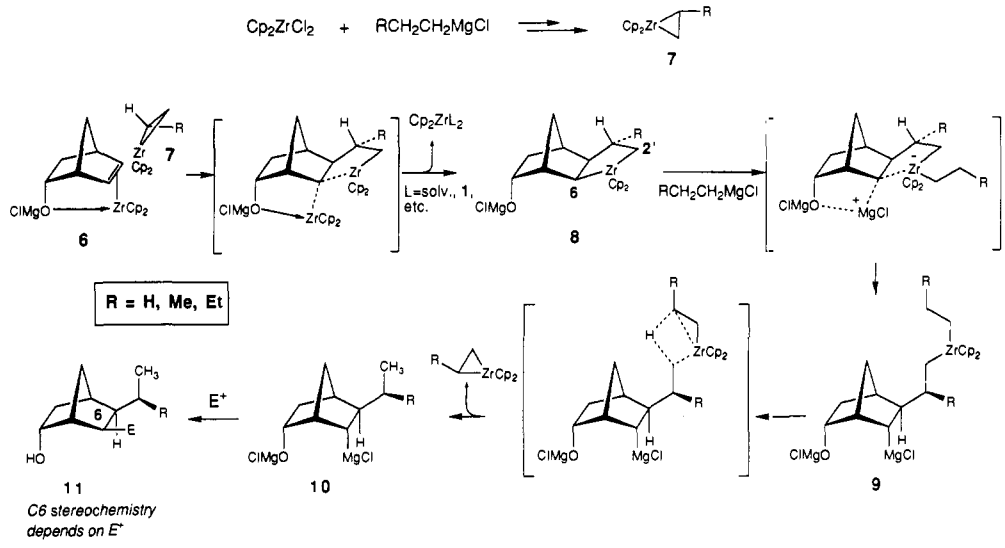
(10) (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544–2546. (b) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336–3346. (c) Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1989**, *111*, 4495–4496. (d) Nugent, W. A.; Taber, D. *J. Am. Chem. Soc.* **1989**, *111*, 6435–6437.

(11) Homoallylic ethers show little selectivity under the stoichiometric conditions; for example, **1b** with 1 equiv of $Cp_2Zr(n\text{-}Bu)_2$ (in THF) affords a 60:40 ratio of regioisomers (C5:C6) in 55% yield. The reaction efficiency is higher than that observed in the catalytic process (27%), presumably since under the catalytic conditions, with an inferior Lewis base (OMEM) and a coordinating solvent, there is little internal coordination and in the stoichiometric reaction there is more of the zirconacyclopropane (**7**, R = Et) available.

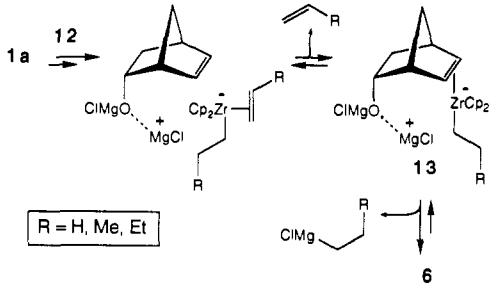
(12) There is no change in yields and selectivities of stoichiometric reactions after 24 h.

(13) (a) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564–8566. (b) Erker, G.; Dorf, U.; Rheingold, A. *Organometallics* **1988**, *7*, 138–143. (c) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120–126. (d) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529–6536. (e) Reference 15.

Scheme I

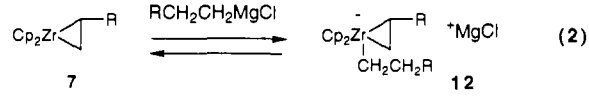


Scheme II



cyclopentane **8**—not **10**—is being quenched.[14] This observation implies that the influence of alkylmagnesium chloride originates from its ability to effect the selective *formation* of the metallacyclopentane and not because it can induce rapid cleavage of the initially (and selectively) formed metallacycle. The stereoselectivity at the secondary alkyl center in the metallacyclopentane (**8**, Scheme I), and the eventual carbometalation product (e.g., **4**), arises from the attack of the zirconacyclopropane such that the alkyl substituent is oriented away from the incoming alkene.[15]

We propose that the influence of additional Grignard reagent stems from generation of the zirconate complex **12** (eq 2, R = H or Me),[16] which may be more susceptible to ligand (alkene) exchange than **7**. Displacement of alkene ligands by **12** (ethylene or propylene for Mg salt of **1a**) would lead to the formation of the zirconocene complex of the reacting alkene, the reactions of which proceed with the degrees of reactivity and selectivity observed in cases where excess alkylmagnesium halide is present.



(2)

The mechanistic details for the abovementioned ligand exchange remain to be clarified; however, one possible scenario is illustrated in Scheme II. Chelation of the ate complex **12** with the heteroatom in **1a** may lead to the stereoselective delivery of the

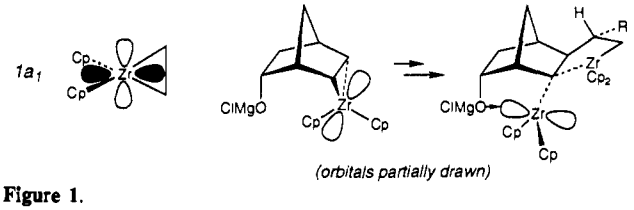


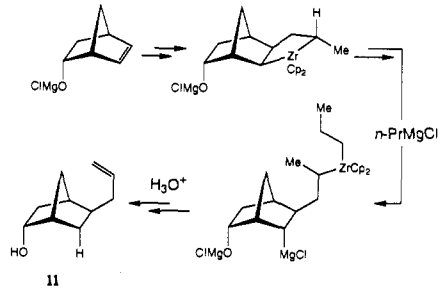
Figure 1.

transition metal to the reacting alkene and formation of **13**, which would then afford **6**. With the parent metallacycle **7**, such association and internal delivery would not be feasible, thus accounting for the greater proclivity of **12** toward ligand exchange and the requirement that additional alkylmagnesium halide be present.

An unsettling aspect of the projected metal–alkene coordination (**6** in Scheme I) is that it would require the involvement of a higher energy orbital of the bound metal. On the basis of studies by Lauher and Hoffmann, the energetically most favorable orbital in zirconium would be of the a_1 symmetry which, as is illustrated in Figure 1, is not well disposed for interaction with heteroatom electrons (orthogonal).[17] It is worthy of note that, as the transition metal shifts or is distorted toward the heteroatom (approaching a structure resembling that illustrated for the intermediate in the conversion **6** + **7** → **8**, Scheme I), the Lewis base–metal interaction

(14) With 4 equiv of *n*-PrMgCl, significant cleavage of **8** (R = Me) is observed (80% yield, C6 deuterium endo).

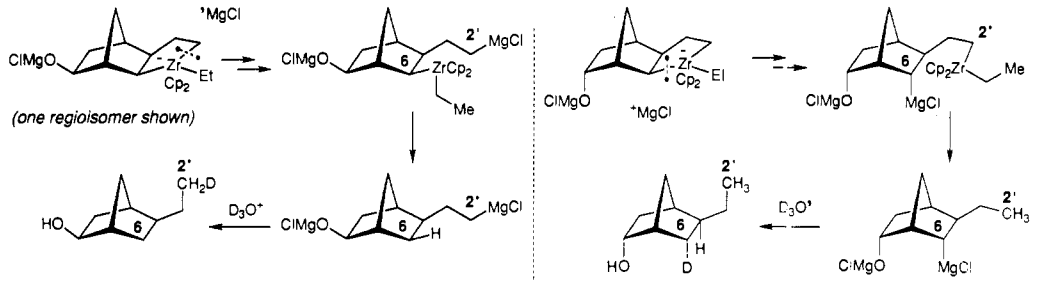
(15) With the higher alkyls of magnesium, it is the more substituted carbon of the zirconacyclopropane that reacts with the alkene. For previous reports on the regioselective alkene additions of unsymmetrical zirconacyclopropanes where insertion occurs predominantly at the more substituted zirconium–carbon bond, see: Swanson, D. R.; Rousset, C. J.; Negishi, E.; Takahashi, T.; Seki, T.; Saburi, M.; Uchida, Y. *J. Org. Chem.* **1989**, *54*, 3521–3523. Addition from the less substituted carbon–zirconium bond would eventually lead to the formation of the allyl adduct **II** (through preferential reductive elimination of the primary C–H bond). Depending on the solvent employed, **II** is generated as the minor product. For example, in the propylmagnesation of **1a** with Et_2O as solvent, only 4% of the allyl adduct is formed (GLC analysis), whereas with THF this product can constitute up to 15% of the reaction mixture. The reason for this solvent dependence is unclear and is under investigation.



(16) Similar zirconate complexes have been broached in connection to the zirconocene-mediated hydrogenation reactions: Takahashi, T.; Suzuki, N.; Kageyama, M.; Nitto, Y.; Saburi, M.; Negishi, E. *Chem. Lett.* **1991**, 1579–1582.

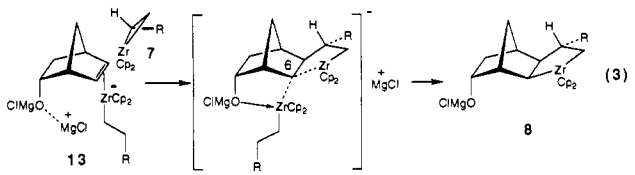
(17) (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742. (b) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; pp 394–398.

Scheme III



(MgClO → Zr, Figure 1) becomes increasingly favorable. Nonetheless, in light of the undesirable disposition of the resident Lewis base toward the LUMO of a symmetrical metal–alkene complex (**6**), it is appropriate to contemplate an alternative mechanism by which the heteroatom induces the observed levels of selectivity without the *direct* intermediacy of **6**.

The initial stages of one such pathway, shown in Scheme II, involve the zirconium–alkene complex **13**. As is demonstrated in eq 3, insertion of the electron-rich olefin of **13** into the zirconacyclopropane **7** would result, via the bimetallic system, in the formation of the intermediate metallacyclopentane **8**. Internal chelation becomes stronger as the transition metal shifts toward the heteroatom (Figure 1), resulting in stabilization of the intermediate bimetallic complex[18] and thus leading to the preferable formation of a C–Zr bond at C6 and the regioselective generation of **8**.



Alkene activation and increase in selectivity could also be due to the interaction of magnesium (rather than zirconocene) with the reacting olefin (i.e., through an intermediate similar to that shown for **8** → **9**, Scheme I). A related mechanism was proposed in 1970 by Felkin and Kaesberg for addition of allylmagnesium bromide to cinnamyl alcohol.[19] The reaction rate was shown to be directly dependent on the amount of $MgBr_2$ present, and with diallylmagnesium, additions proved to be "very slow". A number of experimental data indicate that, in the zirconium-catalyzed carbomagnesations of cyclic homoallylic alcohols and ethers, magnesium salts are not responsible for the postulated internal chelation. When the Mg salt of **1a** is treated with 1 equiv of diethylzirconocene, in addition to the alkoxymagnesium chloride, 2 equiv of $MgCl_2$ is present (from reaction of alkylmagnesium chloride with zirconocene dichloride), yet selectivities are significantly inferior to the catalytic conditions (vide supra). When, instead of alkylmagnesium chloride, various amounts (1–3 equiv) of $MgCl_2$ are added to the Mg salt of **1a** prior to the addition of diethylzirconocene, no change in either reaction efficiency or selectivity is observed. Finally, in contrast to observations of Felkin, under zirconocene catalysis reactions of **1** with dialkylmagnesium reagents are efficient and as selective as those with alkylmagnesium halides; for example, with Et_2Mg, **1a** reacts to >90% conversion within 4 h with 99:1 regioselectivity (C5:C6).[20]

These findings collectively indicate that magnesium halides present in the reaction mixture do not play a significant role in substrate chelation and subsequent enhancement of reactivity and selectivity.

Therefore, our studies illustrate that, whereas zirconacyclopropane addition to the Mg salt of **1a** is nonselective, the derived zirconocene complex (e.g., **13**) is more reactive and undergoes carbomagnesation with high levels of selectivity. In contrast, addition of zirconacyclopropane **7** to the exo bicyclic isomer, or to various extents with **1b** (particularly in THF), proceeds directly and nonselectivity without the aid of a metal–alkene complex.

(2) Regio- and Stereoselective Metallacyclopentane Cleavage. With terminal alkenes, primary carbon–metal bonds are often favored in the carbomagnesation reaction. A significant advantage in using a disubstituted olefin as a mechanistic probe is that the regioselectivity of the carbometalation process can be investigated (the question of whether C–Mg bond forms at the carbon proximal or remote to the heteroatom). The mechanism in Scheme I includes the pathway recently proposed[2b] for the rupture of zirconacyclopentanes by alkylmagnesium halides.[21] However, deuterium labeling experiments demonstrate that the *heteroatom in 1 can strictly control and reverse the mode of metallacyclopentane cleavage.* As is illustrated in Scheme III, in carbomagnesation of *exo*-5-norbornen-2-ol (EtMgCl, 5 mol % Cp_2ZrCl_2), a D_2O/D_2SO_4 quench leads to deuterium incorporation mainly at C2′ (≥95:5, *d*-C2′:*d*-C6; ^2H and ^{13}C NMR analysis). In contrast, with **1a**, D_3O^+ workup affords ≥95% deuterium at C6 (endo).[22] That is, in carbomagnesation of the exo substrate, transmetalation at the less sterically encumbered C2′–Zr bond predominates, affording the primary C2′–Mg bond. With the endo compound, the regiochemical outcome of cleavage is such that the secondary C6–Mg bond is formed.

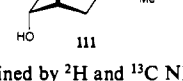
It is reasonable to suggest that with the Mg salt of **1a**,[23] the heteroatom binds and delivers the magnesium ion to initiate a complete reversal in the regioselective metallacyclopentane

(18) For examples of a trigonal bipyramidal methyl group that is bridged by two zirconocene units, see: (a) Waymouth, R. M.; Santesario, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 4050–4051. (b) Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1427–1441. (c) Buchwald, S. L.; Lucas, E. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 397–398.

(19) Felkin, H.; Kaesberg, C. *Tetrahedron Lett.* **1970**, 4587–4590.

(20) Another related observation is that treatment of the Mg salt of **1a** with Cp_2ZrEt_2 (1 h) and then 3 equiv of *n*-BuLi leads to 100% conversion and a 95:5 ratio of C5:C6 alkyl regioisomers (concomitant with the selective formation of *sec*-butyl adducts; GLC analysis). Without addition of *n*-BuLi, 30–40% conversion and 65–70% regioselectivity are obtained. These experiments were performed by Mary Didiuk of these laboratories.

(21) Reaction of an authentic sample of zirconacyclopentane **8** (R = H, from Cp_2ZrEt_2, 200 mol % EtMgCl with Mg salt of **1a**) with CD_3CH_2MgBr (5 equiv, 15 h) results in >95% deuterium incorporation at the methyl group (^{13}C NMR analysis). The β-hydride elimination of **9** (R = Me or Et) occurs predominantly at the methylene and not the methine site (C1′). The latter would afford an alkene adduct such as **III**, which is formed as the minor product (for example, 5% in reaction of **1a** with *n*-PrMgCl, as determined by GLC analysis). As reported recently by Buchwald and Nielsen, the mechanism for release of zirconocene–alkene complex (**9** → **10**, Scheme I) involves a concerted pathway through a four-membered transition structure. Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171–3175. In addition, decomposition of dialkylzirconocenes, such as **9** → **10**, has been shown to proceed by a nondissociative mechanism: Negishi, E.; Swanson, D. R.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1254–1255.

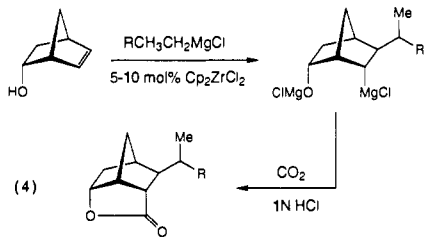


III

(22) Ratios were determined by ^2H and ^{13}C NMR analysis. With **1a**, in reactions with *n*-PrMgCl (not EtMgCl) 15% deuterium at C2′ is observed. However, since <5% protonation at C6 is also detected (^{13}C NMR analysis, 125 MHz), deuterium at C2′ is not the result of nonselective cleavage, but is likely due to quenching of the zirconacyclopentane or the derived magnesiocyclopentane.

(23) Similar observations were made with the derived ethers. For example, D_3O^+ quenching of reaction of **1b** with *n*-BuMgCl, under the catalytic conditions, results in exclusive deuterium incorporation at C6 (as judged by ^{13}C NMR analysis).

cleavage and effect a Mg–Zr exchange with inversion of configuration (**8** → **9**, Scheme I).[24] In support of this hypothesis, we find that, as is illustrated in eq 4, treatment of the carbomagnesation products from **1a** with CO_2, an electrophile known to trap norbornylmagnesium halides with retention,[25] results in the formation of **14** and **15** in 98% and 85% yields, respectively.[26] Control experiments indicate that equilibration does not occur at C6 upon workup; <5% deuterium is observed at C6 of **14** when the reaction is quenched with CO_2 and D_2O/D_2SO_4.



(4)

14 R = H, 98% yield
15 R = Me, 85% yield

In summary, the first examples of catalytic, regio- and stereoselective carbomagnesations with longer chain alkyl Grignard reagents are presented. Excess alkylmagnesium halide is needed if appreciable degrees of reaction selectivity and efficiency are to be achieved. Depending on the amount of Grignard reagent present, either the metallacyclopentane (**8**) or the carbometalation product (**10**) can be obtained selectively. Finally, deuterium labeling experiments indicate that an internal heteroatom controls the mode of cleavage of the intermediate five-membered metallacycle. Further investigation of the transition metal-catalyzed carbomagnesation reaction, both in connection to applications in synthesis and issues of mechanism, particularly in relation to catalytic reactions of acyclic substrates, is in progress and will be the subject of upcoming reports from this laboratory.

Experimental Section

General. All reactions were conducted in oven- (135 °C) and flame-dried glassware under an inert atmosphere of dry argon. Tetrahydrofuran and diethyl ether were distilled from sodium metal/benzophenone ketyl. Cp_2ZrCl_2 was purchased from Boulder Scientific Co. and used without further purification. Ethyl chloride (neat or as 2.0 M Et_2O solution), Mg (turnings), triethylamine, acetic anhydride, and MEM chloride were purchased from Aldrich and used without further purification. Deuterium oxide and sulfuric acid-d_2 were purchased from Norell Chemical Co. and were used as received. Bromoethane-*1,1*-d_2 and bromoethane-*2,2,2*-d_3 were used as received from Merck Sharp & Dohme/Isotopes. Dry CO_2 was obtained from dry ice which was passed through a solution of H_2SO_4 followed by a P_2O_5 trap. Anhydrous CO was passed through $CaCl_2$ before use. 5-Norbornen-2-ol is commercially available (Aldrich) as a mixture of isomers; the endo and exo isomers are separated by silica gel chromatography (6:1, hexanes/EtOAc).

Typical Experimental Procedure for the Zirconium-Catalyzed Butylmagnesation. Alcohol **1a** (99.0 mg, 0.90 mmol) was dissolved in freshly distilled anhydrous Et_2O (3.0 mL). After the solution was cooled to 0 °C, 4.3 mL (1.25 M, 5.37 mmol) of freshly prepared *n*-BuMgCl (in Et_2O) was added in a dropwise fashion. The mixture was then allowed to warm to 25 °C, after which it was charged with Cp_2ZrCl_2 (27.0 mg, 0.09 mmol). The solution was allowed to stir at 25 °C for 40 h. The mixture was cooled to 0 °C and charged with 4.0 mL of 0.1 N HCl. After addition of 25 mL of distilled water and extraction with three 35-mL portions of CH_2Cl_2, the combined organic layers were treated with a saturated solution of NaCl (200 mL) and subsequently dried over anhydrous $MgSO_4$. Removal of solvent and silica gel chromatography (10:1, hexanes/EtOAc) afforded 130 mg (0.77 mmol, 86% yield) of **4a**. GLC analysis, in comparison with an authentic 3:1 regioisomeric mixture obtained from the stoichiometric reaction, indicated >99:1 regiocontrol in favor of **4a**. The minor peaks in the GC spectrum (presumably the corresponding diastereomers) amount to less than 5%. No minor peaks can be detected in the 300- and 500-MHz ^1H NMR spectra (>95% diastereoselectivity).

Typical Experimental Procedure for Stoichiometric (in Zirconium) Carbomagnesation. Cp_2ZrCl_2 (500 mg, 1.71 mmol) was dissolved in 2.4 mL of freshly distilled anhydrous THF and then cooled to −78 °C. To this solution was added *n*-PrMgCl (2.10 mL, 3.15 mmol), and the mixture was allowed to stir for 1 h at −78 °C. (This mixture is a 0.38 M solution of $Cp_2Zr(n\text{-}Pr)_2$ in the presence of 10% $Cp_2Zr(n\text{-}Pr)Cl$ to ensure complete consumption of all of the alkylmagnesium halide.) In a separate flask, **1a** (150 mg, 1.36 mmol) was pretreated with 1 equiv of *n*-PrMgCl (1.09 mL, 1.64 mmol); $Cp_2Zr(n\text{-}Pr)_2$ (first mixture, 3.6 mL, 1.36 mmol) was then added to the magnesium salt of **1a**, and the concoction was allowed to stir for 6 h at 25 °C. The solution was cooled to 0 °C, and the reaction was quenched with HCl (10 mL, 2.0 M). The resulting mixture was washed with three 100-mL portions of CH_2Cl_2, after which the organic layers were washed with 100 mL of a saturated solution of sodium bicarbonate. Drying of organic layers over anhydrous $MgSO_4$ and removal of solvent in vacuo afforded a yellow oil, which was directly treated with Et_3N (1.14 mL, 8.18 mmol), acetic anhydride (0.39 mL, 4.09 mmol), and (dimethylamino)pyridine (10 mg, 0.08 mmol) in 2.0 mL of CH_2Cl_2. After 1 h, the solution was passed through a short column of silica gel (2 cm). Removal of solvent in vacuo and GLC analysis of the resulting residue in comparison with authentic materials indicated 70% conversion and 70:30 regioselectivity in favor of **2a**.

***exo*-5-Isopropyl-*endo*-2-norbornanol (2a):** IR (NaCl) 3350 (br), 2950 (s), 2875 (s), 1470 (s), 1440 (s), 1390 (s), 1350 (s), 1325 (s), 1300 (m), 1280 (m), 1150 (s), 1110 (m), 1100 (m), 1060 (s), 1040 (s), 1000 (s) cm^{-1}; ^1H NMR δ 4.21 (m, 1 H, C*H*OH), 2.24 (s, 1 H, bridge CH), 2.11 (s, 1 H, bridge CH), 1.99 (m, 2 H, exo CH(OH)CH_2 and endo CH(OH)CHCH_2), 1.08 (m, 6 H, endo CH(OH)CH_2, exo CH(OH)CHCH_2, CH(CH$_3$)$_2$, C*H*CH(CH$_3$)$_2$, and bridgehead CH_2), 0.90 (d, 3 H, J = 6.6 Hz, CH_3), 0.82 (d, 3 H, J = 6.4 Hz, CH_3); ^{13}C NMR δ 72.5, 50.4, 42.8, 41.0, 39.5, 34.9, 32.9, 27.4, 21.6, 20.2. Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.74; H, 12.01.

***exo*-5-Isopropyl-*endo*-2-norbornyl (2-methoxyethoxy)methyl ether (2b):** IR (NaCl) 2980 (s), 2890 (s), 1480 (m), 1460 (m), 1370 (m), 1300 (w), 1230 (w), 1180 (s), 1150–1000 (s), 840 (m) cm^{-1}; ^1H NMR δ 4.70 (s, 2 H, $CH_2CH_2OCH_2O$), 4.07 (m, 1 H, CHC*H*OCH$_2$-OCH$_2$CH$_2$OCH$_3$), 3.69 (m, 2 H, OCH$_2$CH_2O), 3.55 (m, 2 H, OCH_2CH$_2$O), 3.38 (s, 3 H, CH_3O), 2.34 (s, 1 H, bridge C*H*), 2.10 (d, 1 H, J = 4.6 Hz, bridge C*H*), 1.92 (m, 2 H, exo CH(OMEM)CH_2 and endo CH(OMEM)CHCH_2), 1.05 (m, 6 H, endo CH(OMEM)CH_2, exo CH(OMEM)CHCH_2, CH(CH$_3$)$_2$, C*H*CH(CH$_3$)$_2$, and bridgehead CH_2), 0.88 (d, 3 H, J = 6.3 Hz, CH_3), 0.80 (d, 3 H, J = 6.3 Hz, CH_3); ^{13}C NMR δ 94.6, 77.2, 71.8, 66.9, 59.0, 50.4, 40.6, 38.8, 38.3, 34.4, 30.9, 28.2, 21.6, 20.2; HR CIMS $C_{14}H_{26}O_3$ + Na requires m/z 265.1780, found 265.1789.

***exo*-5-Isobutyl-*endo*-2-norbornanol (3a):** IR (NaCl) 3320 (br), 2960 (s), 2885 (s), 1460 (s), 1400 (m), 1350 (m), 1320 (m), 1150 (m), 1110 (m), 1080 (m), 1050 (s), 990 (m) cm^{-1}; ^1H NMR δ 4.23 (m, 1 H, CH$_2$CH(OH)), 2.26 (s, 1 H, bridge CH), 2.14 (d, 1 H, J = 5.9 Hz, bridge C*H*), 2.01 (m, 2 H, exo CH(OH)CH_2 and endo CH(OH)-CHCH_2), 1.25 (m, 8 H, endo CH(OH)CH_2, exo CH(OH)CHCH_2, CH(CH$_3$)$_2$, C*H*CH(CH$_3$)$_2$, CH_2CH$_3$, and bridgehead CH_2), 0.86 (t, 3 H, J = 7.1 Hz, CH_3CH$_2$), 0.81 (d, 3 H, J = 6.1 Hz, CH_3CH); ^{13}C NMR δ 72.6, 48.1, 42.9, 41.3, 39.3, 39.1, 35.1, 27.6, 27.4, 16.0, 10.1. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.76; H, 12.16.

***exo*-5-Isobutyl-*endo*-2-norbornyl (2-methoxyethoxy)methyl ether (3b):** IR (NaCl) 2980 (s), 2890 (s), 2200 (w), 1460 (s), 1390 (m), 1380 (m), 1290 (m), 1280 (m), 1240 (m), 1200 (m), 1180 (s), 1110 (s), 1050 (s), 990 (m) cm^{-1}; ^1H NMR δ 4.70 (s, 2 H, OCH_2O), 4.08 (m, 1 H, C*H*OCH$_2$OCH$_2$CH$_2$OCH$_3$), 3.70 (m, 2 H, CH$_3$OCH$_2$CH_2O), 3.56 (m, 2 H, CH$_3$OCH_2CH$_2$O), 3.40 (s, 3 H, CH_3O), 2.36 (t, 1 H, J = 4.6 Hz, bridge CH), 2.11 (d, 1 H, J = 4.9 Hz, bridge CH), 1.92 (m, 2 H, exo CH(OMEM)CH_2 and endo CH(OMEM)CHCH_2), 1.25 (m, 8 H, endo CH(OMEM)CH_2, exo CH(OMEM)CHCH_2, CH(CH$_3$)$_2$, C*H*CH(C-H$_3$)$_2$, CH_2CH$_3$, and bridgehead CH_2), 0.84 (t, 3 H, J = 7.1 Hz, CH_3CH$_2$), 0.78 (d, 3 H, J = 6.1 Hz, CH_3); ^{13}C NMR δ 94.6, 77.3, 71.8, 66.[illegible]9.0, 48.0, 40.6, 39.0, 38.6, 38.4, 34.5, 28.2, 27.5, 16.0, 10.8. HR CI $C_{15}H_{28}O_3^+$ Na requires m/z 279.1936, found 279.1959.

***exo*-5-Ethyl *endo*-2,6-Lactone 14.** Alcohol **1a** (79.1 mg, 0.71 mmol) was dissolved in 4 mL of Et_2O and then cooled to 0 °C. To this solution was added freshly prepared EtMgCl (1.35 mL, 2.15 mmol) in a dropwise fashion. The mixture was allowed to warm to 25 °C, after which Cp_2ZrCl_2 (21.0 mg, 0.07 mmol) was added to the mixture. After 3 h,

(24) When an authentic sample of **8** (R = H or Me) is treated with excess alkylmagnesium halide and then the reaction is quenched with D_2O/D_2SO_4, >95% deuterium incorporation at C6 is observed (endo). It is noteworthy that treatment of **8** (without additional exposure to EtMgCl) with D_3O^+ leads to the formation of >95% deuterium incorporation at C2′ and C6 (exo *d*-C6; ^1H, ^2H and ^{13}C NMR analysis).

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(26) Secondary alkylmagnesium haides are conformationally stable (Whitesides, G. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 4878–4888); *endo*-norbornylmagnesium chloride equilibrates slowly in 24 h at 25 °C (see ref 25). Reaction of **1a** with EtMgCl (10 mol % Cp_2ZrCl_2; CO_2) within 2 h affords >95% yield of **13**.

gaseous CO_2 was introduced into the reaction mixture for 20 min. Subsequent addition of 10 mL of a 1.0 M solution of HCl was followed by allowing the reaction mixture to stir for 15 additional min. Aqueous extraction with three 35-mL portions of CH_2Cl_2, treatment of the organic layers with 30 mL of a saturated solution of $NaHCO_3$, drying of the resultant CH_2Cl_2 solution over $MgSO_4$, and removal of solvent in vacuo afforded a light yellow oil. Purification of this residue by silica gel chromatography (10:1, hexanes/EtOAc) afforded 116 mg (0.69 mmol, 98% yield) of the desired product as a clear viscous oil: IR (NaCl) 2960 (s), 2940 (s), 2860 (s), 2850 (m), 1780 (s), 1720 (s), 1480 (m), 1440 (m), 1380 (s), 1310 (m), 1180 (s) cm^{-1}; ^1H NMR δ 4.73 (dd, 1 H, J = 7.8, 4.8 Hz, C*H*(OCO)), 3.10 (dt, 1 H, J = 4.9, 1.2 Hz, C*H*C(O)), 2.25 (s, 1 H, bridge CH), 2.13 (d, 1 H, J = 4.4 Hz, bridge CH), 1.76 (m, 3 H, CH(OCO)CH_2 and C*H*CH_2CH$_3$), 1.14 (m, 2 H, bridgehead CH_2), 1.34 (dt, 2 H, J = 7.3, 6.3 Hz, CH_2CH$_3$), 0.94 (t, 3 H, J = 7.3 Hz, CH_3); ^{13}C NMR δ 180.7, 80.4, 49.7, 45.9 (2C), 40.6, 38.8, 34.8, 27.5, 11.7. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.18; H, 8.52.

***exo*-5-Isopropyl *endo*-2,6-lactone 15**: IR (NaCl) 3560 (w), 2950 (s), 2850 (s), 1780 (s), 1720 (s), 1640 (m), 1480 (s), 1440 (m), 1380 (m), 1360 (m), 1350 (s), 1320 (m), 1300 (s), 1270 (m), 1180 (s), 1115 (s), 1090 (s), 1020 (s), 990 (s) cm^{-1}; ^1H NMR δ 4.75 (dd, 1 H, J = 7.8, 5.1 Hz, C*H*(OCO)), 3.11 (t, 1 H, J = 4.8 Hz, C*H*C(O)), 2.44 (d, 1 H, J = 2.7 Hz, bridge CH), 2.28 (d, 1 H, J = 4.9 Hz, OCHCH$_2$C*H*), 1.50 (m, 6 H, CH_2CHO, bridgehead CH$_2$, C*H*(CH$_3$)$_2$, C*H*CH(CH$_3$)$_2$), 0.99 (d, 3 H, J = 6.1 Hz, CH_3CH), 0.94 (d, 3 H, J = 6.3 Hz, CH_3CH); ^{13}C NMR δ 180.0, 80.5, 55.9, 46.1, 44.8, 39.1, 39.0, 34.7, 30.9, 20.7, 20.4; HR CIMS $C_{11}H_{16}O_2$ + 1 requires m/z 181.1228, found 181.1225.

Ketone I. Alcohol **1a** (150 mg, 1.36 mmol) was dissolved in THF (5.0 mL), and *n*-PrMgCl (1.10 mL, 1.63 mmol) was added to the solution. $Cp_2Zr(n\text{-}Pr)_2$ (1.36 mmol, prepared at −78 °C according to the procedure mentioned above) was added to the original mixture at 25 °C. The solution was allowed to stir for 5 h, cooled to 0 °C, and treated with gaseous CO. The mixture was allowed to warm to 25 °C under CO atmosphere for 2 h. The reaction was quenched upon addition of a 5-mL portion of a 2.0 M solution of HCl. Subsequent extraction with three 100-mL portions of CH_2Cl_2, drying of organic layers over anhydrous $MgSO_4$, and removal of solvent in vacuo afforded a yellow oily residue. Silica gel chromatography (3:1, hexanes/EtOAc) yielded 147 mg of ketone I (0.82 mmol, 60% yield): IR (NaCl) 3434 (brm), 3426 (m), 3419 (m), 3408 (m), 1731 (s) cm^{-1}; ^1H NMR δ 4.24 (dt, 1 H, J = 9.8, 3.9 Hz, C*H*OH), 2.92 (d, 1 H, J = 9.3 Hz, C*H*C(O)), 2.55 (d, 1 H, J = 3.9 Hz, CH(OH)C*H* (bridge CH)), 2.29 (dd, 1 H, J = 17.0, 7.3 Hz, exo CH_2C(O)), 2.15 (d, 1 H, J = 6.3 Hz, bridge CH), 2.01 (m, 2 H, endo CH_2C(O), exo CH_2CH(OH)), 1.94 (dd, 1 H, J = 8.8, 7.3 Hz, CH$_3$CHC*H*), 1.71 (m, 1 H, C*H*(CH$_3$)), 1.19 (d, 3 H, J = 6.9 Hz, CH$_3$), 1.12 (dp, 1 H, J = 3.9, 1.9, 11.2 Hz, bridgehead CH anti to ketone), 0.85 (dt, 1 H, J = 13.2, 3.4 Hz, bridgehead CH syn to ketone); ^{13}C NMR δ 222.9, 71.0, 52.3, 47.9 (2C), 45.7, 41.9, 38.0, 34.1, 33.6, 21.6; HR EIMS $C_{11}H_{16}O_2$ requires m/z 180.1150, found 180.1150.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank the referees for their helpful comments.

Supplementary Material Available: Spectra of deuterium labeling experiments in reactions of **1a** and the corresponding exo alcohol (5 pages). Ordering information is given on any current masthead page.

An NMR Study of the Formation of Silyloxonium Ions by Using Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate as Counteranion[1]

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Abstract: The capability of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) as a counteranion for organosilicenium ions was investigated by NMR spectroscopy. Although reactions of hydrosilanes with trityl-TFPB did not give the corresponding silicenium ions as long-lived species in dichloromethane-d_2, the reactions produced rather stable silyloxonium ions in the presence of ethers at low temperatures. The evidence for the formation of cyclic silyloxonium ions was obtained by monitoring the reaction of 3-ethoxypropylsilanes with trityl-TFPB by NMR spectroscopy. The use of TFPB as a non-nucleophilic counteranion was crucial for the formation of the silyloxonium ions; silyl perchlorates did not show significant interaction with ethers.

Introduction

The question of the existence of silicenium ions[2] in solution or in the solid state has received much attention in recent years. Lambert et al.[3] have claimed by means of conductance, cryoscopic molecular weight, and ^1H, ^{13}C, and ^{15}N NMR spectroscopy that triphenylsilyl and trimethylsilyl perchlorates are ionic species in sulfolane and acetonitrile as well as in highly diluted dichloromethane. On the other hand, Olah et al.[4,5] have argued against this conclusion; they have concluded that these silyl perchlorates exist as covalent esters both in solution and in the solid state by ^{29}Si and ^{35}Cl NMR spectroscopy and X-ray crystallography.

Perchlorate ion used in the previous studies would not be suitable for a counteranion of silicenium ions, because of the high oxo-

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(2) The nomenclature for trivalent silico cation has been controversial. Lambert, Barton, and some others have used the term *silylenium*, since the divalent species corresponding to *carbene* is *silylene*. However, *silylene* should have a logical relationship to *methylene* rather than *carbene*; the term corresponding to *carbene* should be *silicene*. On this basis, we prefer here to use *silicenium* as the general term for trivalent silicocations after Olah et al.

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